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# Raman Spectroscopy Evaluation of Polyvinylchloride Structure

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**Abstract.** In this work we investigated Raman spectra of a number of industrial grades of polyvinylchloride powder and films, prepared from solutions in tetrahydrofuran and acetophenone. The number and spectral characteristics of the Raman lines in the spectral regions of the C-Cl stretching vibrations and in the region of the C-H and CH<sub>2</sub> stretching vibrations were evaluated.

## 1. Introduction

Polyvinylchloride (PVC) is one of the most widely used commercial polymers, and the field of its application continues to expand rapidly. Effective development of state-of-art functional materials, such as PVC-based nanocomposites, copolymers, blends and fabrics, subjected to special kinds of treatment, requires elaboration of new, more informative approaches in PVC structure evaluation.

It is well known that PVC macromolecules can be found in two ordered configurations – syndiotactic and isotactic. Macromolecules of syndiotactic PVC in *trans*-conformation can form the orthorhombic crystalline lattice with the unit cell, containing two monomer units from each of two macromolecules, passing through the unit cell. The amorphous phase of PVC consists of macromolecules in atactic configuration and macromolecules with segments in syndiotactic and isotactic configurations in various conformational states.

Industrial PVC is characterized by variety of configurational and conformational macromolecular states and defects and, as a consequence, by very low degree of crystallinity. Thus, the best way to evaluate PVC structure is to apply vibrational spectroscopy, the unique feature of which is very high informativity relative to different configurational and conformational states of macromolecules.

Raman spectroscopy is a powerful method to analyze polymer structure in terms of chemical and phase compositions, contents of different configurational and conformational states, and orientational order of macromolecules. Most of Raman spectroscopic methods of PVC structure analysis in terms of the phase composition, configurational and conformational order [1 - 13], macromolecular orientation [14 - 18] and the degree of degradation/dehydrochlorination [19 - 26] were published long time ago and were based on the spectral analysis using Lorentz shape of the lines. Therefore, re-examination of the already existing methods and development of modern computer-based approaches with emphasis



on exact evaluation of number and spectral characteristics of PVC Raman-active lines are extremely important.

Furthermore, most of the published investigations deal with the region of the C-Cl stretching vibrations ( $500 - 800 \text{ cm}^{-1}$ ) and do not consider other PVC lines, which can be also useful for structural analysis. For example, the most intense PVC lines are observed in the region of the C-H and  $\text{CH}_2$  stretching vibrations ( $2750 - 3100 \text{ cm}^{-1}$ ), and, therefore, this spectral range is very attractive for study of PVC samples with highly luminescent additives, such as fillers, impurities or residues of solvent or catalyst or for study of small amounts of PVC in polymer blends.

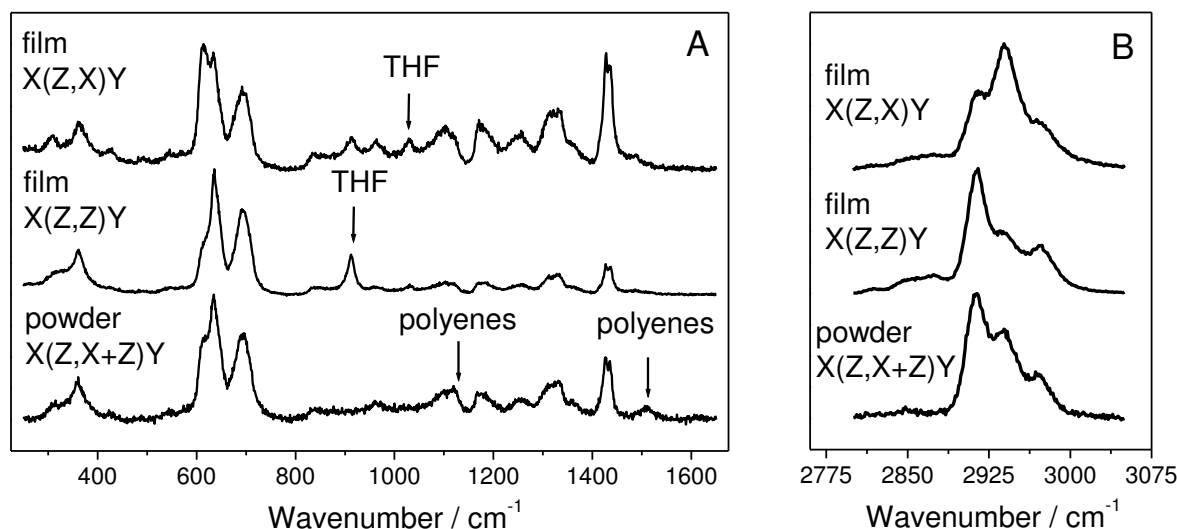


Figure 1. Raman spectra of the PVC powder (Aldrich) and the film, prepared from this powder using THF: A – spectral region  $250 - 1650 \text{ cm}^{-1}$ , B - spectral region  $2800 - 3050 \text{ cm}^{-1}$ .

The selection rules and symmetry of PVC Raman- and IR-active vibrations were calculated for an isolated molecule [3, 4] and for the orthorhombic crystalline phase [1, 2]. The  $A_1$ ,  $A_2$ ,  $B_1$ , and  $B_2$  symmetry vibrations should appear in the Raman spectrum of syndiotactic PVC macromolecule in *trans*-conformation. Due to intermolecular interaction in the orthorhombic unit cell, each Raman line of the two syndiotactic molecules, passing through the unit cell, splits into two lines. Therefore, Raman spectrum of the PVC orthorhombic crystalline phase composes of  $A_g$ ,  $B_{1g}$ ,  $B_{2g}$ , and  $B_{3g}$  symmetry vibrations.

In this work we present an extensive study of Raman spectra of a number of industrial grades of PVC powder and investigation of polarized Raman spectra of films, prepared from solutions in tetrahydrofuran (THF) and acetophenone. Investigation of polarized Raman spectra allows determining depolarization ratios and, thus, the symmetry of Raman-active vibrations. Besides, analysis of polarized spectra is useful for determination of the number and the spectral characteristics of Raman lines, because of significant simplification of the spectra due to damping of the lines with particular symmetry at specified directions of polarization of the exciting and scattered radiation.

## 2. Experimental

We studied Raman spectra of three industrial grades of PVC powder - 389293 Aldrich, E-62 (emulsion polymerization), C-7059 (suspension polymerization), and spectra of thick fully-isotropic and optically-transparent films, prepared from PVC solution in THF and acetophenone by evaporation of solvent at room temperature. The film thickness (exceeding  $200 \mu$ ) was enough to exclude molecular orientation, which can form in thin films due to boundary effects. In accordance with data of X-ray analysis and differential scanning calorimetry techniques, the degree of crystallinity of all the samples under investigation was less, than 5 %.

Raman setup included two lasers with 488 and 532 nm excitation lines, double monochromator, and water-cooled photomultiplier. Raman spectra were recorded in the 90°-scattering geometry with spectral resolution of 5 cm<sup>-1</sup>. Spectra of the films were recorded with parallel (X(Z,Z)Y geometry) and crossed (X(Z,X)Y geometry) directions of polarization of the laser and scattered radiation. Raman spectra of powders were recorded without polarizer - X(Z,X+Z)Y geometry. The reason was strong depolarization of the laser and scattered light due to multiple reflections and refractions during scattering in the powder. Because of the optical properties of the diffraction gratings, used in the monochromator, in the absence of depolarization effects, the non-polarized spectra were similar to the spectra recorded in the X(Z,Z)Y geometry.

Spectral characteristics of the Raman lines were calculated based on the deconvolution analysis of the experimental spectra, using in-house software. The shape of each line was described by the weighted sum of Lorentz and Gauss functions:

$$y = A_0 \left[ \mu \frac{2}{\pi} \frac{\gamma}{4(\nu - \nu_0)^2 + \gamma^2} + (1 - \mu) \frac{2\sqrt{\ln 2}}{\sqrt{\pi}\gamma} \exp\left(-\frac{4\ln 2}{\gamma^2}(\nu - \nu_0)^2\right) \right]$$

where  $0 \leq \mu \leq 1$ ;  $A_0$ ,  $\nu_0$  and  $\gamma$  - the integral intensity, peak position, and full width at half maximum, respectively. The baseline was described as a second-order polynomial. All the parameters (except  $\mu$ ) were allowed to vary without any constraints.

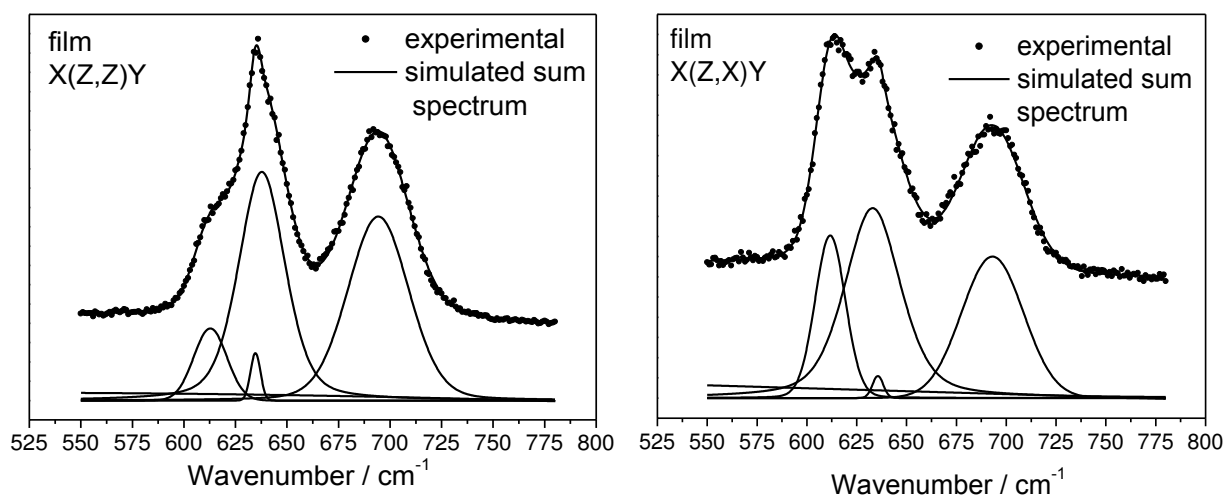


Figure 2. Examples of the deconvolution of the PVC polarized Raman spectra in the region of the C-Cl stretching vibrations: PVC film, prepared from solution of the Aldrich powder in THF, the 532 nm excitation laser line: A – X(Z,Z)Y geometry, B - X(Z,X)Y geometry.

### 3. Results and Discussion

As a typical example, figure 1 shows Raman spectra of the PVC industrial powder (Aldrich) and the film, prepared from THF solution of this PVC in two most informative spectral regions. We did not observe any Raman-active lines with noticeable intensity in the spectral range from 1650 to 2800 cm<sup>-1</sup>. All the spectra, presented in figure 1, are recorded using the laser line at 532 nm for excitation. The film was completely isotropic and optically transparent, that allows us to record polarized Raman spectra of very high quality. For the sake of clarity, in each spectral region Raman spectra were normalized to the intensity of the most intense line after subtraction of a linear background. The Raman spectra, recorded in the X(Z,X+Z)Y and X(Z,Z)Y geometry, were normalized to the peak intensity of the line at about 633 and 2914 cm<sup>-1</sup>, respectively, and the Raman spectra, recorded in the X(Z,X)Y geometry, were normalized to the peak intensity of the line at about 612 and 2940 cm<sup>-1</sup>, respectively.

The first feature to be noted is obvious difference in the film spectra, recorded with parallel (X(Z,Z)Y geometry) and crossed (X(Z,X)Y geometry) directions of polarization of the laser and scattered radiation (figure 1 (A,B)). The second feature is the presence of additional lines in the film spectra compared with the powder spectrum (two most prominent of them at about 911 and 1030  $\text{cm}^{-1}$  are marked in figure 1). We assign these lines to the Raman-active vibrations of THF, remained in the film [27, 28].

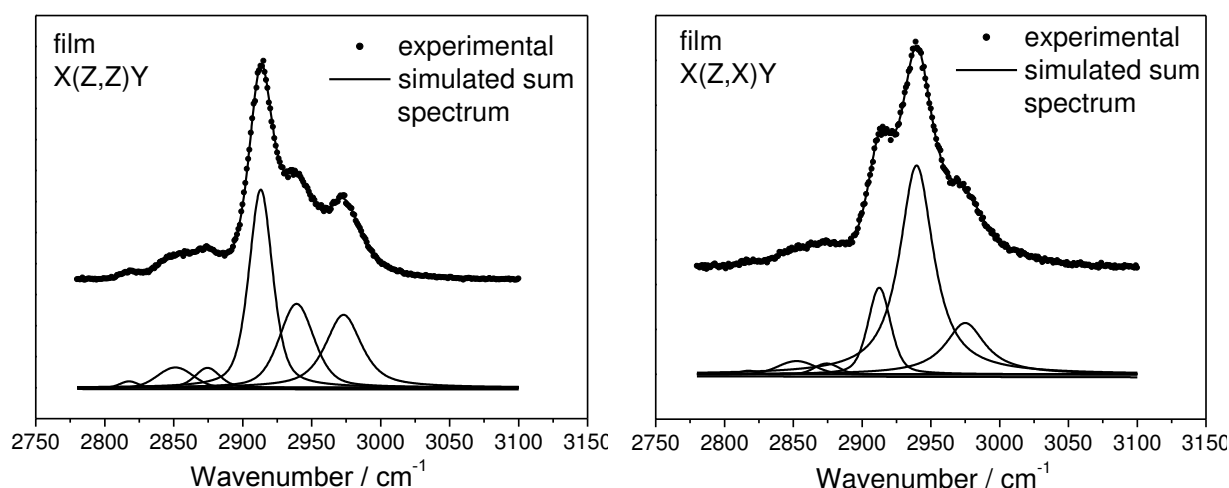


Figure 3. Examples of the deconvolution of the PVC polarized Raman spectra in the region of the C-H and  $\text{CH}_2$  stretching vibrations: PVC film, prepared from solution of the Aldrich powder in THF, the 532 nm excitation laser line: A – X(Z,Z)Y geometry, B - X(Z,X)Y geometry.

**Table 1.** Spectral characteristics of the PVC Raman lines in the C-Cl stretching region.

Sample / geometry	Line N 1			Line N 2			Line N 3			Line N 4		
	$\nu_0$ ( $\text{cm}^{-1}$ )	$\gamma$ ( $\text{cm}^{-1}$ )	$I_0^a$	$\nu_0$ ( $\text{cm}^{-1}$ )	$\gamma$ ( $\text{cm}^{-1}$ )	$I_0$	$\nu_0$ ( $\text{cm}^{-1}$ )	$\gamma$ ( $\text{cm}^{-1}$ )	$I_0$	$\nu_0$ ( $\text{cm}^{-1}$ )	$\gamma$ ( $\text{cm}^{-1}$ )	$I_0$
488 nm												
Aldrich powder / non- polarized	614	18	0.12	639	31	0.44	696	38	0.43	637	7	0.01
C-7059 powder / non- polarized	613	18	0.16	639	30	0.38	696	38	0.45	637	5	0.02
E-62 powder / non-polarized	614	19	0.15	639	29	0.39	696	39	0.45	637	7	0.01
532 nm												
Film (Aldrich/THF) / X(Z,Z)Y	615	19	0.09	640	27	0.46	696	35	0.44	637	6	0.02
Film (Aldrich/THF) / X(Z,X)Y	614	18	0.19	635	33	0.48	695	37	0.33	638	6	0.01
Aldrich powder / non- polarized	613	18	0.14	638	31	0.42	695	38	0.43	636	7	0.01

<sup>a</sup> $I_0$  - integral intensity, normalized to the total integral intensity of the Raman scattering in the C-Cl stretching region (sum of the integral intensities of four lines).

Two weak features in the Aldrich powder spectrum – the lines at about 1120 and 1510  $\text{cm}^{-1}$  (the first is manifested only as a high-frequency shoulder of the PVC line at 1101  $\text{cm}^{-1}$ ) are related to vibrations of conjugated polyenes [19 - 26], formed in PVC due to dehydrochlorination. Due to the resonance nature of Raman scattering for polyenes, at the 532 nm line excitation, the basic contribution to the Raman scattering at 1510  $\text{cm}^{-1}$  comes from polyenes with 15 conjugated double bonds. We did not reveal the line at 1510  $\text{cm}^{-1}$  in the Aldrich film spectra, but the additional scattering at about 1120  $\text{cm}^{-1}$  was clearly detected. Also, in the spectra of our samples we did not observe the lines at 2143, 2625, 3017, and 3175  $\text{cm}^{-1}$ , which were also noticed in Raman spectrum of dehydrochlorinated PVC [20].

Comparison of the spectra of the PVC powders (389293 Aldrich, E-62, and C-7059) did not reveal any significant difference, except presence of the lines at 1120 and 1510  $\text{cm}^{-1}$  in the Aldrich powder spectrum. Raman spectra of the films, prepared with THF and acetophenone, differ in presence of the residual THF lines in the spectrum of the first film and in presence of very intense background in the spectrum of the second film.

**Table 2.** Spectral characteristics of the PVC Raman lines in the region of the C-H and  $\text{CH}_2$  stretching vibrations<sup>b</sup>.

Sample / geometry	Line N 1			Line N 2			Line N 3		
	$\nu_0$ ( $\text{cm}^{-1}$ )	$\gamma$ ( $\text{cm}^{-1}$ )	$I_0^c$	$\nu_0$ ( $\text{cm}^{-1}$ )	$\gamma$ ( $\text{cm}^{-1}$ )	$I_0$	$\nu_0$ ( $\text{cm}^{-1}$ )	$\gamma$ ( $\text{cm}^{-1}$ )	$I_0$
488 nm									
Aldrich powder / non-polarized	2940	32	0.41	2914	20	0.35	2974	25	0.19
C-7059 powder / non-polarized	2940	30	0.39	2914	20	0.38	2974	26	0.19
E-62 powder / non-polarized	2940	34	0.45	2914	20	0.36	2975	25	0.14
532 nm									
Film (Aldrich/THF) / X(Z,Z)Y	2941	30	0.24	2915	20	0.41	2975	31	0.25
Film (Aldrich/THF) / X(Z,X)Y	2942	29	0.62	2915	19	0.14	2977	35	0.19
Aldrich powder / non-polarized	2940	32	0.48	2914	20	0.33	2975	23	0.14

**Table 2.** (continuation).

Sample / geometry	Line N 4			Line N 5		
	$\nu_0$ ( $\text{cm}^{-1}$ )	$\gamma$ ( $\text{cm}^{-1}$ )	$I_0$	$\nu_0$ ( $\text{cm}^{-1}$ )	$\gamma$ ( $\text{cm}^{-1}$ )	$I_0$
488 nm						
Aldrich powder / non-polarized	2849	25	0.04	2819	10	0.01
C-7059 powder / non-polarized	2847	25	0.04	2819	9	0.01
E-62 powder / non-polarized	2852	27	0.05	2821	12	0.01
532 nm						
Film (Aldrich/THF) / X(Z,Z)Y	2853	30	0.05	2820	15	0.01
Film (Aldrich/THF) / X(Z,X)Y	2854	31	0.03	2819	13	0.003
Aldrich powder / non-polarized	2850	30	0.04	2818	19	0.01

<sup>b</sup>Data for the line N 6 – see text.

<sup>c</sup> $I_0$  - integral intensity, normalized to the total integral intensity of the Raman scattering in the C-H and  $\text{CH}_2$  stretching region (sum of the integral intensities of five or six lines).

Figures 2 and 3 present examples of the deconvolution of the PVC polarized Raman spectra in the region of the C-Cl stretching vibrations (figure 2) and in the region of the C-H and CH<sub>2</sub> stretching vibrations (figure 3) in two scattering geometries. It was revealed that the number of the lines is equal to 4 in the region of the C-Cl stretching vibrations and to 5 or 6 in the region of the C-H and CH<sub>2</sub> stretching vibrations. Tables 1 and 2 summarize spectral characteristics of the PVC Raman lines in these spectral regions, calculated for the PVC powders and films for two excitation wavelengths. Data for the film, prepared using acetophenone, are not included because of low signal-to-noise ratio in this spectrum. It can be seen that the calculated spectral characteristics for the spectra of different samples are in good agreement. It should be noted that all the parameters (except  $\mu$ ) were allowed to vary without any constraints. In the polarized spectra of the film we observed the redistribution of the scattered intensity due to the symmetry properties of the vibrations.

In [5] it was stated that in the C-Cl stretching region of PVC spectra (500 – 800 cm<sup>-1</sup>) 9 Raman-active lines (+ 4 additional lines with unknown assignment) can be found with pure Lorentz line shapes. Among them are 2 lines, attributed to syndiotactic molecules in the crystalline phase (corresponding to the C-Cl stretching vibration at 608 cm<sup>-1</sup> with B<sub>3g</sub> symmetry and the C-Cl stretching vibration at 638 cm<sup>-1</sup> with A<sub>g</sub> symmetry), and 7 lines, attributed to syndiotactic and isotactic molecules in different conformational states in the non-crystalline phase. Authors of the work [5] supposed that integral intensities of the lines in the C-Cl stretching region of PVC spectra can be used to calculate the degree of crystallinity and tacticity of PVC.

**Table 3.** Depolarization ratios  $R=I_{ZZ}/I_{XZ}$  and assignment [5, 9, 13, 15] of the PVC Raman lines.

Wavenumber (cm <sup>-1</sup> )	R, integral intensity	R, peak intensity	Assignment
614	0.42	0.43	non-crystalline phase, syndiotactic molecules in trans-conformation
637 (weak)	0.10	0.09	crystalline phase, the C-Cl stretching vibration, A <sub>g</sub>
639	0.20	0.16	non-crystalline phase, isotactic molecules in TGTG*TG conformation
696	0.14	0.15	non-crystalline phase, isotactic molecules in TGTGTG conformation
2819	0.09	0.10	the C-H stretching vibration
2851	0.12	0.11	the symmetric CH <sub>2</sub> stretching vibration
2877	0.08	0.09	THF
2914	0.07	0.08	the asymmetric CH <sub>2</sub> stretching vibration
2940	0.52	0.43	the asymmetric CH <sub>2</sub> stretching vibration
2975	0.15	0.12	the C-H stretching vibration

In the Raman spectra of our samples in this region we have found only 4 lines - three strong lines at 614, 639 and 696 cm<sup>-1</sup> and very weak line at 637 cm<sup>-1</sup>. The first three lines are clearly visible in the spectra of all the samples under study (figure 1A). The fourth line was introduced to describe additional scattering, which was observed in all the sample spectra and was not described by the model of three lines.

Because of the very low degree of crystallinity of our samples, three strong lines were assigned to the non-crystalline phase. This assumption is confirmed by relatively high values of width of these lines (table 1). The weak and relatively narrow line at 637 cm<sup>-1</sup> was assigned to the orthorhombic crystalline phase.

Thus, instead of 13 lines, which were found in the C-Cl stretching region of PVC spectra in [5], we observed only four lines. It should be noted that in our deconvolution analysis the shape of each line was described by the weighted sum of Lorentz and Gauss functions, instead of pure Lorentz function, used in [5].

In [5, 6] it was stated that Raman spectra in the region of the C-H and CH<sub>2</sub> stretching vibrations (2800 – 3050 cm<sup>-1</sup>) weakly depend on the PVC configurational and conformational composition. However, there is little information on the number and assignment of Raman-active lines in this region. Probably, it is due to the fact that analysis of this spectral range is complicated because of strong overlapping of the lines. That is why we used assignment of the IR-active PVC lines for this region (table 3, [9, 13]). This assignment is in good agreement with the results of theoretical calculation of the vibrational spectrum of the syndiotactic PVC chain in trans-conformation [7].

In this region we found 5 lines, corresponding to the PVC vibrations, and one THF line [27, 28]. The last line was observed only in the spectra of the film, prepared from solution of the Aldrich powder in THF. The last line has the following spectral characteristics in the X(Z,Z)Y / X(Z,X)Y spectra: peak position – 2877 / 2876 cm<sup>-1</sup>, width - 21 / 21 cm<sup>-1</sup>, normalized integral intensity I<sub>0</sub> - 0.04 / 0.02. It is important to note that all the PVC lines are clearly observed in the all sample spectra without spectrum deconvolution (figure 1B).

Using polarized Raman spectra of the isotropic and transparent film, obtained from solution of the Aldrich powder in THF, we calculated the depolarization ratios of the lines in the regions of the C-Cl stretching vibrations and the C-H and CH<sub>2</sub> stretching vibrations. These values as well as the assignment of the PVC lines, taken from literature, are presented in table 3.

Authors of work [6] published values of depolarization ratios of Raman lines in the C-Cl stretching region for a melt-formed isotropic PVC film. We cannot directly compare the values of the depolarization ratios, published in [6] and obtained in this work, because authors of the work [6] used 14 lines in the spectrum deconvolution analysis and, thus, the peak positions and widths of the lines are different for their and our results. However, the line at 614 cm<sup>-1</sup> with width of about 18 cm<sup>-1</sup> and depolarization ratio of 0.43, which was found in the spectra of our samples, most probably corresponds to the line at 615 cm<sup>-1</sup> with width of about 20 cm<sup>-1</sup> and depolarization ratio of 0.63. Besides, our line at 639 cm<sup>-1</sup> with width of about 30 cm<sup>-1</sup> and depolarization ratio of 0.16, is similar to the line at 636 cm<sup>-1</sup> with width of about 25 cm<sup>-1</sup> and depolarization ratio of 0.15 from work [6]. In addition, our line at 696 cm<sup>-1</sup> with width of about 38 cm<sup>-1</sup> and depolarization ratio of 0.15, can correspond to the line at 698 cm<sup>-1</sup> with width of about 35 cm<sup>-1</sup> and depolarization ratio of 0.18.

#### 4. Conclusion

In this work we investigated Raman spectra of a number of industrial grades of PVC powder and films, prepared from solutions in tetrahydrofuran and acetophenone. Raman spectra of three grades of PVC powder, prepared by suspension polymerization and emulsion polymerization and bought from Aldrich Company, turn out to be very similar. Characteristics of the Raman lines, calculated using deconvolution analysis of two most important spectral regions of PVC Raman spectrum – the regions of the C-Cl stretching vibrations and the C-H and CH<sub>2</sub> stretching vibrations, were identical for all powders and films under study. We assigned the lines at 614, 639 and 696 cm<sup>-1</sup> to vibrations of PVC macromolecules in the non-crystalline phase and the line at 637 cm<sup>-1</sup> – to macromolecular vibrations in the orthorhombic crystalline phase.

In Raman spectra of the film, prepared from solution of the Aldrich powder in THF, we observed a number of THF lines. It is an indication of presence of residues of the solvent in the film.

Analysis of polarized spectra of the PVC films allows evaluating unambiguously the number and the spectral characteristics of the PVC Raman lines. These data are very useful for more accurate assignment of the PVC Raman lines to particular vibrations and can be applied for evaluation of structure of different PVC-based materials. Analysis of other spectral regions in PVC Raman spectrum is in progress.

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